



Zeolitic imidazolate framework-68 as an efficient heterogeneous catalyst for chemical fixation of carbon dioxide



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ABSTRACT

An efficient heterogeneous catalyst, namely, zeolitic imidazolate framework-68 (ZIF-68), was developed for the synthesis of cyclic carbonate from CO₂ and styrene oxide in the absence of any solvents or co-catalysts under mild reaction conditions (120 °C and 1.00 MPa). The textural properties of the ZIF-68 catalyst were determined by the powder X-ray diffraction, N₂ adsorption–desorption and thermal analysis. The acid–base property of ZIF-68 catalyst was investigated by NH₃ and CO₂ temperature-programmed desorption methods. The results indicate that the yield of cyclic carbonate reached up to 93.3% after 12 h in the mild reaction conditions. Moreover, the ZIF-68 catalyst could be successfully reused for three times without any significant loss in catalytic activity.

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1. Introduction

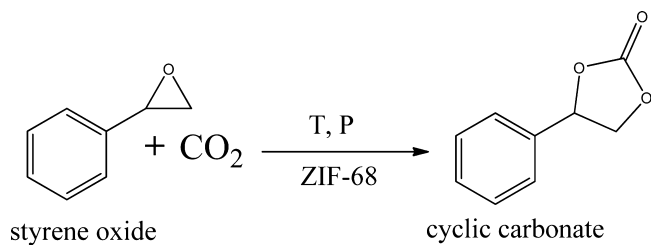
Carbon dioxide (CO₂) is one of the greenhouse gases that have posed great threat to environment. Recently, the chemical fixation of CO₂ into useful chemicals has attracted great interest [1–3]. One of the most effective approaches to transform CO₂ into useful chemicals is to utilize CO₂ and styrene oxide to produce five-membered cyclic carbonates (Scheme 1). The produced cyclic carbonate can be used as polar aprotic solvents, electrolytes, and intermediates in a wide range of chemical reactions [4]. Various homogeneous catalysts, such as transition metal complexes [5], ionic liquid catalysts [6], and quaternary ammonium salts [7], have been studied in the cyclic addition of CO₂ and styrene oxide. Considering that the homogeneous catalyst is difficult to separate and recover, several heterogeneous catalysts have been suggested for the cyclic addition reactions. Most of these catalysts, however, suffer from low activities or harsh reaction conditions such as, elevated temperature, high pressure of CO₂, and the necessity of organic solvent or co-catalyst [8–10]. To date, investigating an environmentally benign heterogeneous catalyst that is highly effective under mild conditions still remains a challenge [11].

Metal organic frameworks (MOF) has emerged as a novel kind of porous crystalline materials with excellent properties, such as uniform microspores, accessible pore volumes, and large surface areas [12], making them potentially interesting candidates for gas storage [13], gas separation [14], magnetism [15], and especially as catalysts [16–19]. MOF materials, including Mg-MOF-74 [20], Co-MOF-74 [8], and MOF-5 [21], have been well-studied in the CO₂ fixation reaction. However, these MOF catalysts are sensitive to water and air, limiting their further applications. Zeolitic imidazolate frameworks (ZIF), a subclass of MOF, are one of the potentially interesting catalyst candidates because of their exceptional chemical and thermal stabilities [22]. Miralda et al. [23] studied the activity of ZIF-8 in the cyclic addition of CO₂ and epichlorohydrin, and the conversion of epichlorohydrin was 65.5% while the chloropropene carbonate selectivity was 63.4%. In addition, Carreon et al. [24] also researched the catalytic performance of ZIF-8 in the synthesis of cyclic carbonate from CO₂ and styrene oxide, and showed that the yield to styrene carbonate was only 53.0% at 100 °C. Besides, the ZIF-8 catalyst lost its distinctive crystalline nature and catalytic performance after recycling.

Thus, finding other alternatives remains a challenge when ZIF-8 still cannot conquer the stability problem for the synthesis of cyclic carbonate. Recently, Woo et al. [25] demonstrated that ZIF-68 (Scheme 2) has extraordinary adsorption capacity of CO₂ by Grand-Canonical Monte Carlo and Molecular-Dynamics Simulations. ZIF-68 with GME topology is composed of one 2-nitroimidazole and one benzimidazole per Zn in an asymmetric

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Scheme 1. Synthesis of cyclic carbonate from CO₂ and styrene oxide.

unit, displaying large pores with diameter of 10.3 Å and accessible through apertures of 7.5 Å as well as exceptional chemical and thermal stabilities [26]. These materials with higher CO₂ adsorption capacity may possess better catalytic activities for CO₂ cyclic addition reaction [24]. Unfortunately, research on ZIF-68 materials for CO₂ fixation is scarce. Herein, we first synthesized ZIF-68 through hydrothermal method, and used it to catalyze the cyclic addition of CO₂ and styrene oxide. Interestingly, the ZIF-68 materials showed excellent catalytic performance and recycle ability.

2. Experimental

2.1. General material and characterization

All the chemicals were purchased from Aldrich Chemical Co. and were used without further purification, unless otherwise stated. Powder X-ray diffraction (XRD) was carried out on a MSAL-XD2 X-ray diffractometer operating at a voltage of 40 kV and a current of 25 mA, with Cu K α radiation. The data were collected at room temperature with a 5° step size in 2θ , 2θ from 5° to 50°. N₂ adsorption–desorption isotherm and pore size distribution of the materials were measured with an ASAP 2020 sorptometer analyzer (Micrometitics Company) at 77 K using liquid nitrogen as coolant. The catalyst was degassed at 150 °C for 3 h before analysis. Thermal gravimetric analysis–differential scanning calorimetry (TGA-DSC) was recorded on a Netzsch STA 409 thermoanalyzer. Approximately 5 mg catalyst was filled into an alumina crucible and heated in a continuous-flow of nitrogen gas with a ramp rate of 10 °C/min from 40 °C up to 800 °C. The acid–base property of ZIF-68 was measured by NH₃-TPD and CO₂-TPD using the AutoChem II 2920 instrument, with helium as a carrier gas. After pretreatment at 150 °C for 3 h, the samples were cooled down to room

temperature and saturated with CO₂ (or NH₃). Subsequently, the physically absorbed CO₂ or NH₃ were removed by flowing helium. Finally, the desorption process was started from 50 °C to 400 °C at a heating rate of 5 °C/min, and monitored by a thermal conductivity detector.

2.2. Preparation of ZIF-68 catalyst

ZIF-68 was prepared by hydrothermal method. A solid mixture of zinc nitrate hexahydrate ([Zn(NO₃)₂] \cdot 6H₂O, 3 mmol), benzimidazole (C₇H₆N₂, 4 mmol), and 2-nitroimidazole (C₃H₃N₃O₂, 7 mmol) was dissolved in N,N-dimethylformamide (DMF, 50 mL), then sealed in a 100 mL Teflon container. The container was maintained in the oven at 100 °C for 72 h. After the reaction, the sample was cooled down to room temperature. The product was washed with DMF (3 \times 10 mL) and ethanol (95%, 3 \times 10 mL), and the obtained yellow polyhedral crystals were finally dried overnight at 150 °C (yield: 83.8% based on benzimidazole).

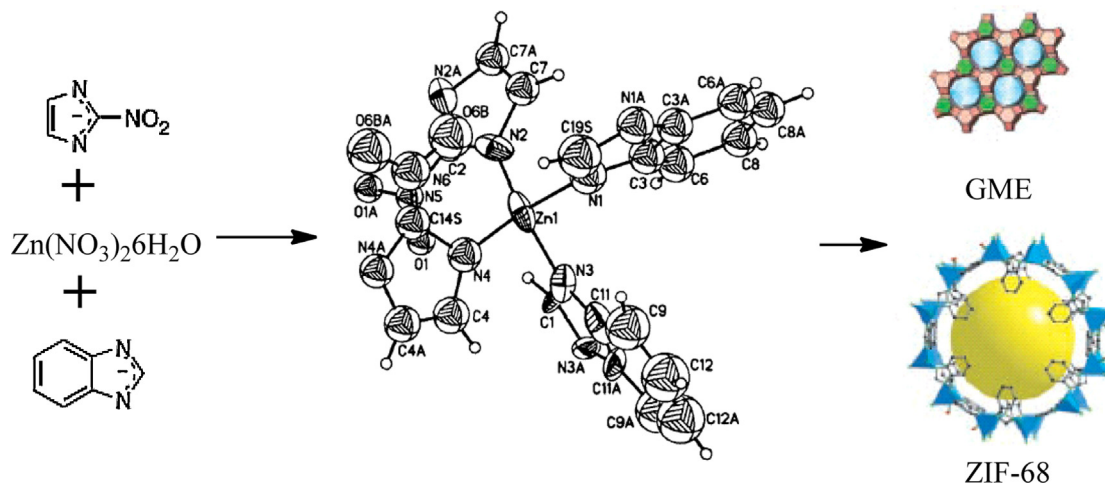
2.3. General procedure for the cyclic addition reaction of CO₂ and styrene oxide

The cyclic addition reaction was carried out in a 100 mL stainless steel autoclave equipped with a magnetic stirrer. The catalyst (0.100 g, pretreated for 3 h at 150 °C), biphenyl (0.222 g) as internal standard, and styrene oxide (0.848 g) were first placed in the autoclave. Subsequently, CO₂ was introduced into the reactor until reaching the desired pressure. The reactor was then heated to a desired temperature for several hours under vigorous stirring. After the reaction, the autoclave was cooled down to room temperature, and the un-reacted CO₂ was slowly released. The product was then diluted with DMF and filtered before GC analysis (Agilent 7890A, HP-5 column: 30 m, 0.320 mm, 0.250 μ m) using an internal standard technique. In the catalyst recycling process, ZIF-68 was separated by centrifugation, washed using ethanol (95%, 3 \times 10 mL), then dried in air at 150 °C.

3. Results and discussion

3.1. Characterization of ZIF-68 catalyst

The textural properties of the ZIF-68 catalyst were determined by the powder X-ray diffraction, N₂ adsorption–desorption and



Scheme 2. Synthesis and topology structure of ZIF-68: the largest cage is shown with Zn₄ tetrahedra in blue, the yellow ball is placed in the structure for clarity and to indicate space in the cage (C, black; N, green; O, red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

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